

## The Raman Spectra and Molecular Constants of the Hexafluorides of Sulfur, Selenium and Tellurium

DON M. YOST, CARSTEN C. STEFFENS AND SIEGFRIED T. GROSS, *Gates Chemical Laboratory, California Institute of Technology\**

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The Raman spectra of the gaseous and liquid hexafluorides of sulfur, selenium and tellurium were determined (Table I). Three lines for each substance were observed and this is the number permitted by the selection rules for a regular octahedral molecule. Frequency formulae based on central forces were derived, and these, together with the appearance of the spectra, were used to assign the observed frequencies to the proper modes of vibration. Estimates of the magnitudes of the forbidden frequencies were made. A provisional value of  $-238,000$  cal. is given for the free energy of formation of  $\text{SF}_6$  (g) at  $25^\circ$ .

### INTRODUCTION

THE hexafluorides of the sulfur group elements have been shown by electron diffraction experiments to consist of highly symmetrical molecules, the six fluorine atoms occupying the corners of a regular octahedron with the remaining atom at the center.<sup>1</sup> No spectroscopic measurements to determine the fundamental molecular frequencies have been made, and further information regarding bond strengths and thermodynamic quantities requires such data. As one step in obtaining such material, the Raman spectra of these substances in both liquid and gaseous forms were determined.

Redlich, Kurz and Rosenfeld<sup>2</sup> have derived, as a function of central force constants, formulae for the fundamental modes of vibration of the regular octahedral molecule, but they oversimplified the problem in ignoring the forces present in the equilibrium positions of the atoms. It was therefore necessary to treat the problem more thoroughly. The results of both the theoretical and experimental studies are presented in this paper.

We wish to express here our appreciation to Professor Roscoe G. Dickinson for valuable suggestions made in connection with the tech-

nique for determining the Raman spectra of gases, and to Dr. E. B. Wilson, Jr., who applied Placzek's<sup>3</sup> theory of scattering to deduce the selection and polarization rules for the octahedral type molecule.

### THEORETICAL

The methods of general dynamics which were developed for the treatment of systems involving more coordinates than degrees of freedom are commonly applied only in case the differential equations of constraint are non-integrable. The same methods are applicable regardless of the integrability of the equations of constraint; but in the integrable cases, as many coordinates as there are equations of constraint can be eliminated, thereby reducing the number of differential equations. If the physical system is highly symmetrical, the corresponding high symmetry of the differential equations may compensate the greater number of equations in the set, as was pointed out by Routh.<sup>4</sup> Since the system considered in this paper is highly symmetrical, the procedure usually applied to non-holonomic systems will be used.

The Lagrangian equations of motion for a non-holonomic system are:

\* Contribution No. 400.

<sup>1</sup> Pauling and Brockway, *Proc. Nat. Acad.* **19**, 68 (1933).

<sup>2</sup> Redlich, Kurz and Rosenfeld, *Zeits. f. physik. Chemie* **B19**, 231 (1932).

<sup>3</sup> Cf. Debye, *The Structure of Molecules*, p. 86, Blackie and Son, London, 1932.

<sup>4</sup> E. J. Routh, *Advanced Rigid Dynamics*, p. 31, Macmillan and Co., N. Y., 4th Ed., 1884.

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = \sum_{j=1}^m \lambda_j \frac{\partial f_j}{\partial q_i},$$

where  $f_j = 0$  for  $j = 1, 2, \dots, m$  are the  $m$  equations of constraint, and the  $\lambda_j$ 's are  $m$  undetermined multipliers. The  $n$  equations of motion plus the  $m$  equations of constraint determine the  $n$  coordinates and  $m$   $\lambda_j$ 's.

An isolated system of point particles, where  $L$  equals  $T - V$  and is not a function of the time, has six integrals of linear and angular momentum, providing six equations of constraint. These momenta will be assumed zero. The motion of the system will be described with  $s$  sets of rectangular coordinates, derivable from one another by translation, whose origins are at the positions of the particles when the system is in an equilibrium configuration.

The potential energy  $V$  may be expanded in a Maclaurin's series in  $n$  variables about the equilibrium configuration. Third and higher powers are neglected. The condition that  $\partial V / \partial q_i = 0$  in an equilibrium configuration does not follow in general from the equations of motion, since these partial derivatives are related, not to the total force along the corresponding coordinates, but only to that part of the force due to reactions included in  $L$  as distinguished from reactions included in the equations of constraint. If, however, an equilibrium configuration of the system is unaffected by the absence of the constraints, or, from another viewpoint, if the constraints exert no forces in the equilibrium configuration, then in that configuration  $\partial V / \partial q_i = 0$ . These partial derivatives are therefore the negatives, not only of the components of that part of the forces included in  $L$ , but also of the total forces along the corresponding coordinates. In the systems of interest, the potential energy is  $2V = \sum_{i=1}^n \sum_{j=1}^n b_{ij} q_i q_j$ .

Since the kinetic energy  $T$  of the system is the sum of the kinetic energies of the particles composing it, and since the coordinates for each particle are orthogonal, no cross-products will appear. The kinetic energy is  $2T = \sum_{i=1}^n a_i \dot{q}_i^2$  where the  $a_i$ 's are constants.

The equations of constraint are homogeneous linear functions of the coordinates,  $f_j = \sum_{i=1}^n \lambda_{ij} q_i = 0$ . The undetermined multipliers may be

written as  ${}_0\lambda_j + {}_1\lambda_j$  where  ${}_0\lambda_j$  is the value of  $\lambda_j$  in the equilibrium configuration.

The equations of motion are solved by the usual substitution  $q_i = A_i e^{\mu t}$  and  ${}_1\lambda_i = -M_i e^{\mu t}$ . The resulting relations are:

$$(a_i \mu^2 + b_{ii}) A_i + \sum_{\substack{j=1 \\ j \neq i}}^n b_{ij} A_j + \sum_{r=1}^6 r f_r M_i = 0$$

$$i = 1, 2, \dots, n,$$

$$\sum_{i=1}^n r f_i A_i = 0 \quad r = 1, 2, \dots, 6.$$

The  ${}_0\lambda_r$ 's are all zero since the equations of motion must be satisfied when the variables and their derivatives are all zero.

The secular determinant is bordered by six rows and six columns of constants. It is of the  $(n+6)$ th order and of the  $(n-6)$ th degree in the variable,  $\mu^2$ , which is confined to the non-zero terms of the principal diagonal. Since a row or column from the border may be used as an operator without disturbing any of the bordering elements, and since these elements are simple, the determinant is comparatively easy to factor. The secular determinant of a system of seven particles arranged in a regular octahedron is a "block circulant," and is immediately factorable into three determinants, each of order  $(n+6)/3$ .<sup>5</sup>

The seven particles, 0, 1,  $\dots$ , 6, are placed in a rectangular coordinate system at 000,  $a00$ ,  $0a0$ ,  $\bar{a}00$ ,  $0\bar{a}0$ ,  $00a$ , and  $00\bar{a}$ , respectively.  $k_{01}$ ,  $k_{12}$ , and  $k_{24}$  denote force constants due to reactions between the central and a peripheral particle, between two adjacent peripheral particles, and between two opposite peripheral particles, respectively.  $m_0$  and  $m_1$  denote the mass of the central and of any peripheral particle, respectively.  $-b$ ,  $-h$ , and  $-j$  denote ratios of forces to corresponding equilibrium distances, where the forces are those at equilibrium due to reaction between the central and a peripheral particle, between two adjacent peripheral particles, and between two opposite peripheral particles, respectively. There is a relation,  $b = -4h - 2j$ , between these constants.

The kinetic and potential energies of the system for infinitesimal displacements and velocities are given by the following equations.

<sup>5</sup> Muir and Metzler, *Theory of Determinants*, p. 485, privately printed, Albany, N. Y., 1930.

$$2T = m_0(\dot{x}_0^2 + \dot{y}_0^2 + \dot{z}_0^2) + m_1(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 + \dot{x}_2^2 + \dot{y}_2^2 + \dots + \dot{z}_6^2),$$

$$\begin{aligned} 2V = & k_{01}[(x_1 - x_0)^2 + (x_3 - x_0)^2 + (y_2 - y_0)^2 + (y_4 - y_0)^2 + (z_5 - z_0)^2 + (z_6 - z_0)^2] + b[(x_2 - x_0)^2 + (x_4 - x_0)^2 \\ & + (x_5 - x_0)^2 + (x_6 - x_0)^2 + (y_1 - y_0)^2 + (y_3 - y_0)^2 + (y_5 - y_0)^2 + (y_6 - y_0)^2 + (z_1 - z_0)^2 + (z_2 - z_0)^2 \\ & + (z_3 - z_0)^2 + (z_4 - z_0)^2] + (k_{12}/2)[(x_1 - y_1 - x_2 + y_2)^2 + (x_1 - z_1 - x_5 + z_5)^2 + (x_1 + y_1 - x_4 - y_4)^2 \\ & + (x_1 + z_1 - x_6 - z_6)^2 + (y_2 - z_2 - y_5 + z_5)^2 + (x_2 + y_2 - x_3 - y_3)^2 + (y_2 + z_2 - y_6 - z_6)^2 + (x_3 - z_3 - x_6 + z_6)^2 \\ & + (x_3 - y_3 - x_4 + y_4)^2 + (x_3 + z_3 - x_5 - z_5)^2 + (y_4 + z_4 - y_5 - z_5)^2 + (y_4 - z_4 - y_6 + z_6)^2] \\ & + (h/2)[(x_1 + y_1 - x_2 - y_2)^2 + (x_1 - z_1 - x_6 + z_6)^2 + (x_1 - y_1 - x_4 + y_4)^2 + (x_1 + z_1 - x_5 - z_5)^2 \\ & + (y_2 + z_2 - y_5 - z_5)^2 + (x_2 - y_2 - x_3 + y_3)^2 + (y_2 - z_2 - y_6 + z_6)^2 + (x_3 + z_3 - x_6 - z_6)^2 + (x_3 + y_3 - x_4 - y_4)^2 \\ & + (x_3 - z_3 - x_5 + z_5)^2 + (y_4 - z_4 - y_5 + z_5)^2 + (y_4 + z_4 - y_6 - z_6)^2] + h[(x_2 - x_5)^2 + (x_5 - x_4)^2 + (x_4 - x_6)^2 \\ & + (x_6 - x_2)^2 + (y_1 - y_6)^2 + (y_6 - y_3)^2 + (y_3 - y_5)^2 + (y_5 - y_1)^2 + (z_1 - z_2)^2 + (z_2 - z_3)^2 + (z_3 - z_4)^2 \\ & + (z_4 - z_1)^2] + k_{24}[(x_1 - x_3)^2 + (y_2 - y_4)^2 + (z_5 - z_6)^2] + j[(x_2 - x_4)^2 + (x_5 - x_6)^2 + (y_1 - y_3)^2 + (y_5 - y_6)^2 \\ & + (z_1 - z_3)^2 + (z_2 - z_4)^2]. \end{aligned}$$

The six integrals of linear and angular momenta equated to zero give the six following equations.

$$\begin{aligned} m_0 x_0 + m_1(x_1 + x_2 + x_3 + x_4 + x_5 + x_6) &= 0, & y_5 - y_6 - z_2 + z_4 &= 0, \\ m_0 y_0 + m_1(y_1 + y_2 + y_3 + y_4 + y_5 + y_6) &= 0, & x_5 - x_6 - z_1 + z_3 &= 0, \\ m_0 z_0 + m_1(z_1 + z_2 + z_3 + z_4 + z_5 + z_6) &= 0, & x_2 - x_4 - y_1 + y_3 &= 0. \end{aligned}$$

The secular determinant is set up from these equations and solved. The roots determine the following six frequencies, the multiplicity being given by the figure in parenthesis.

$$4\pi^2\nu_1^2(1) = (k_{01} + 4k_{12} + 2k_{24})/m_1, \quad (1) \quad 4\pi^2\nu_3^2(3) = (2k_{12} - 2h)/m_1, \quad (3)$$

$$4\pi^2\nu_2^2(2) = (k_{01} + k_{12} + 2k_{24} + 3h)/m_1, \quad (2) \quad 4\pi^2\nu_4^2(3) = (k_{12} + h - 2j)/m_1, \quad (4)$$

$$\begin{aligned} 4\pi^2\nu_{5,6}^2(3) &= \frac{1}{2m_0m_1} \{A \pm [A^2 + 4m_0(m_0 + 6m_1)(-k_{01}k_{12} + 3k_{01}h + 2k_{01}j + 4(2h + j)(k_{12} + h))]^{\frac{1}{2}}\}, \\ A &= (m_0 + 2m_1)k_{01} + 3m_0k_{12} - (m_0 + 16m_1)h - 2(m_0 + 4m_1)j, \end{aligned} \quad (5)$$

$$\nu_1^2 = \nu_2^2 + (3/2)\nu_3^2. \quad (6)$$

Another set of frequency formulae for the octahedral  $XY_6$  molecule was derived by Dr. E. B. Wilson, Jr., using a very restricted type of valence-force potential function involving only three constants,  $k_{01}$  the  $X-Y$  force constant,  $p$  the interaction constant for the effect of extension of the  $X-Y$  bond, and  $k_\varphi$  the constant for the bending of the valence bonds. A more thorough treatment would, of course, introduce further constants. The formulae are the following:

$$4\pi^2\nu_1^2(1) = (k_{01} + 4p)/m_1, \quad (7) \quad 4\pi^2\nu_3^2(3) = 4k_\varphi/m_1, \quad (9)$$

$$4\pi^2\nu_2^2(2) = (k_{01} - 2p)/m_1, \quad (8) \quad 4\pi^2\nu_4^2(3) = 2k_\varphi/m_1, \quad (10)$$

$$4\pi^2\nu_{5,6}^2(3) = \frac{1}{6m_1(1 + 4m_1/m_0)} \left\{ B \pm \left[ B^2 - 48 \left( 1 + \frac{4m_1}{m_0} \right) \left( 1 + \frac{6m_1}{m_0} \right)^2 k_{01}k_\varphi \right]^{\frac{1}{2}} \right\}, \quad (10)$$

$$B = 24 \frac{m_1^2}{m_0^2} k_{01} + 6 \left( 1 + \frac{4m_1}{m_0} \right)^2 k_\varphi + 2 \left( 1 + \frac{4m_1}{m_0} \right) (k_{01} + k_\varphi), \quad (11)$$

$$\nu_3/\nu_4 = 2^{\frac{1}{2}}. \quad (12)$$

Of these six frequencies,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are permitted by the Raman selection rules, and the two latter will be depolarized equally with  $\rho=6/7$ . The modes of vibration are pictured in Fig. 1 and are in agreement with those described by Redlich, Kurz and Rosenfeld.<sup>2</sup>

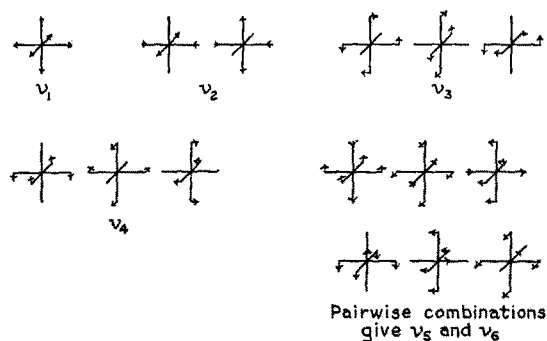


FIG. 1. Fundamental modes of vibration of regular octahedral model of  $XY_6$ .

#### EXPERIMENTAL

The hexafluorides were prepared by treating elementary sulfur, selenium, and tellurium with gaseous fluorine. The methods of purification have been described elsewhere.<sup>6</sup> About two days were required for the preparation of each compound.

In the experiments on the liquids, the material was contained in a Pyrex glass tube 1 cm in diameter equipped at one end with a plane glass window and at the other with a right cone of black nickel-oxide Pyrex glass. The tube was supported vertically in a Dewar flask silvered on one-half of its circumference. Cooled alcohol or ice-water served as low temperature baths. In all cases the liquids were under pressures varying from five to nine atmospheres. The selenium and tellurium compounds were run at  $0^\circ$ , and that of sulfur at  $-50^\circ$ . A mercury arc in Pyrex served as a source of radiation.

The strongest Raman line appeared after an exposure of twenty minutes, but to obtain all of the lines two or three hours were necessary. In no case were more than three lines observed resulting from a single exciting frequency. For a given exposure time, the Raman lines from tellurium hexafluoride were the most intense and those from the sulfur compound the least.

In the experiments on the gaseous hexafluorides, quartz was used throughout. The

spectrograph contained in it a dish of mercury whose vapor served to absorb a large fraction of the 2537Å radiation used to excite the spectra. The tube containing the gases was 2.5 cm in diameter, and 30 cm long. It was equipped with a 1.3 cm diameter window at one end, and a right cone, covered with optical black paint to prevent reflections, at the other. The gases were present at a pressure of about 75 lbs./sq. in.

The lengths of the exposures for the gases varied from a half hour to thirty hours. Tellurium hexafluoride yielded three Raman lines. The one of greatest  $\Delta\nu$  was strong and sharp with only a trace of diffuseness on the long wave-length side. The weakest line had a well-defined center and faint, diffuse wings. The line of least  $\Delta\nu$  was broad ( $19\text{ cm}^{-1}$ ) and uniformly intense over most of its width, and appeared also as anti-Stokes radiation. The other two gases yielded only one strong sharp line each. For a given length of exposure, the most intense lines were obtained from tellurium hexafluoride and the least intense from the sulfur compound.

The lines obtained from the liquids were appreciably broader than those from the gases. The accuracy attained for the former was about  $\pm 3\text{ cm}^{-1}$  and for the strongest line of the latter  $\pm 0.1\text{ cm}^{-1}$ .

#### RESULTS OF EXPERIMENTS

The results of the experiments are presented in Table I, together with the interatomic distances obtained from electron diffraction experiments.<sup>1</sup> The numbers in parenthesis adjoining the symbols  $\nu$  are multiplicities, those adjoining the frequency values are relative intensities.

Only three lines are permitted by the selection rules and this is the number observed.

As the table shows the frequency  $\nu_1$  has nearly the same value for the gases as for the liquids, a result that is usually found for nonpolar substances.<sup>7</sup> The highly symmetrical hexafluoride molecules evidently do not interact with each

<sup>6</sup> Yost and Claussen, J. Am. Chem. Soc. 55, 885 (1933).

<sup>7</sup> Kohlrausch, *Der Smekal Raman Effekt*, p. 126, Julius Springer, Berlin, 1931.

TABLE I. *The Raman frequencies of sulfur, selenium and tellurium hexafluorides.*

Sub- stance	State	$\nu_1(1)$ cm <sup>-1</sup>	$\nu_2(2)$ cm <sup>-1</sup>	$\nu_3(3)$ cm <sup>-1</sup>	$M-F$ A	$I \times 10^{40}$
SF <sub>6</sub>	Liquid	776(10)	642(2)	522(2)		
	Gas	772.4			1.58	311.5
SeF <sub>6</sub>	Liquid	710(10)	662(2)	405(2)		
	Gas	708.0			1.70	362.5
TeF <sub>6</sub>	Liquid	697(10)	672(2)	316(4)		
	Gas	701.2(10)	674.4(1)	313*(4)	1.84	425.0

 $M-F$  = distance from S, Se, or Te to F. $I$  = moment of inertia in g·cm<sup>2</sup>.\* The width is about 19 cm<sup>-1</sup>.

other in such a way as to affect appreciably the valence forces, although the bonds themselves may be ionic in character.

The assignment of the strongest line from each substance to the completely symmetrical mode of vibration,  $\nu_1(1)$  is in accord with the theory<sup>3</sup> and is almost certainly correct. In the case of the gases, the strongest line is also sharp with only a trace of diffuseness on the long wave-length side. This indicates a  $Q$  branch and is to be expected from the mode of vibration,  $\nu_1(1)$ . The weakest line from tellurium hexafluoride was assigned to  $\nu_2$ , and has a well-defined center with less intense, diffuse wings on either side which were, however, rendered somewhat indistinct by the continuous background. The broad line is moderately intense and is assigned to  $\nu_3$ . The broadness is doubtless due to unresolved rotational structure, and the uniform intensity over its width indicates the presence of  $P$ ,  $Q$  and  $R$  branches. These considerations, together with the relative magnitudes of the frequencies to be expected from the modes of vibration involved, would seem to confirm the assignments given to the lines. To render them more certain the constant-free relation, Eq. (6), between the allowed frequencies was employed.

From the relation,  $\nu_1^2 = \nu_2^2 + (3/2)\nu_3^2$ , it is evident that  $\nu_1$  is the greatest of the three frequencies. It was found that the best agreement was obtained when the smallest frequency was assigned to  $\nu_3$ . The values of  $(\nu_2^2 + (3/2)\nu_3^2)^{1/2}$  are from 10 percent to 17 percent greater than those observed for  $\nu_1$ , the best agreement being obtained with tellurium hexafluoride. The assign-

ments are, therefore, in agreement with the best available criteria. It must be pointed out that polarization experiments would be of little assistance in this case since the depolarization factor,  $\rho$ , will be the same for  $\nu_2$  and  $\nu_3$ .

#### THE FORCE CONSTANTS AND FORBIDDEN FREQUENCIES

Both sets of frequency formulae were used to estimate the magnitudes of the forbidden frequencies. The values so calculated are to be regarded as rough approximations only. They would serve as a guide in the analysis of absorption spectra.

The data are insufficient to determine all the constants of Eqs. (1-5). From the relation discovered by Professor R. M. Badger<sup>8</sup> of this laboratory it is possible to determine, at least approximately, the values of  $k_{01}$ , and, with less certainty,  $k_{12}$ .  $k_{24}$  is certainly small and is disregarded.  $h$  may be calculated from  $\nu_2$  alone, and elementary inverse square law considerations show that  $j = h/(2)^{1/2}$ .  $k_{01}$  and  $k_{12}$  were used to calculate  $\nu_1$  in order to test the approximate correctness of the constants. The agreement with experiment is not exact but is satisfactory. The results of the calculations are represented in Table II. The negative values for  $h$  and  $j$  indicate the existence of repulsive forces between fluorine atoms.

TABLE II. *Estimated force constants and forbidden frequencies. Eqs. (1-5) (central forces).*

Sub- stance	$k_{01}$ $\times 10^{-5}$	$k_{12}$ $\times 10^{-5}$	$\nu_1$ calc.	$\nu_1$ obs.	$-h$ $\times 10^{-5}$	Estimated for- bidden frequencies		
						$\nu_4$	$\nu_5$	$\nu_6$
SF <sub>6</sub>	5.9	0.50	844	772	1.0	280	620	1510
SeF <sub>6</sub>	5.8	0.36	807	708	0.55	230	570	960
TeF <sub>6</sub>	5.9	0.26	790	701	0.28	190	420	850

The  $\nu$ 's are expressed in cm<sup>-1</sup> and the constants in dynes/cm.

Similar calculations were made using Eqs. (7-11). The three constants were determined in this case directly from the experimental data. The results are presented in Table III.

It does not appear possible to make a definite choice between the kinds of bonds postulated in

<sup>8</sup> Private communication.

TABLE III. *Estimated forbidden frequencies Eqs. (7-11) (valence bonds).*

Sub- stance	$k_{01}$ $\times 10^{-5}$	$p$ $\times 10^{-5}$	$k_{\phi}$ $\times 10^{-5}$	$\nu_4$ cm $^{-1}$	$\nu_5$ cm $^{-1}$	$\nu_6$ cm $^{-1}$
SF $_6$	5.30	0.344	0.765	370	540	970
SeF $_6$	5.15	0.123	0.460	286	430	650
TeF $_6$	5.23	0.086	0.274	222	310	610

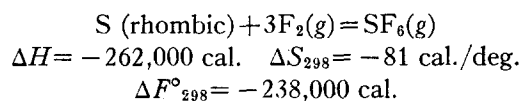
deriving the two sets of frequency formulae. That the bonds are not of the extreme ionic type seems likely in virtue of the fact that the spectra are readily obtained.

Of the three frequencies forbidden in the Raman effect,  $\nu_5$  and  $\nu_6$  should be observed in infrared absorption experiments. Specific heat measurements on the gaseous hexafluorides would also add considerably to our knowledge concerning the magnitudes of the unknown frequencies.

#### THERMODYNAMIC CONSTANTS

The virtual entropy of sulfur hexafluoride may be expressed as  $S^*_{298} = S_a + S_f$ , where  $S_f$  is the entropy associated with the forbidden frequencies and  $S_a$  the remaining entropy. The value of  $S_a$  is 64.6 cal./deg., and it was calculated from the data in Table I. The symmetry number is 24.  $S_f$

was estimated by using the first set of calculated values for the forbidden frequencies, and has the provisional value 5.9 cal./deg.  $S^*_{298}$  becomes then 70.5 cal./deg. The entropy of fluorine is 48.0 cal./deg.,<sup>9</sup> and that of rhombic sulfur is 7.6 cal./deg.<sup>10</sup> at 25° and 1 atmosphere. The heat of formation of sulfur hexafluoride at constant pressure and 25° is 262,000 cal.<sup>6</sup> When these values are combined, the following equation can be written.



It is believed that the error in this provisional value of  $\Delta F^{\circ}_{298}$  is due principally to that in  $\Delta H$ , namely,  $\pm 3000$  cal. As an application of this free energy value, it may easily be shown that sulfur hexafluoride has a large tendency to hydrolyze when brought into contact with water, but due to the extreme slowness of the reaction, no hydrolysis is observed. However, it may be predicted that no hexafluoride will result when sulfuric and hydrofluoric acids are mixed, and this is in agreement with experiment.

<sup>9</sup> Yost and Hatcher, J. Chem. Educ. **10**, 330 (1933).

<sup>10</sup> Lewis and Randall, *Thermodynamics*, p. 464, McGraw-Hill Book Co., N. Y., 1923.